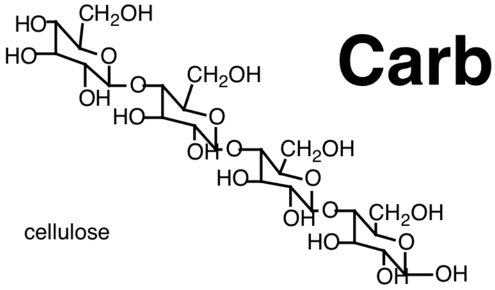
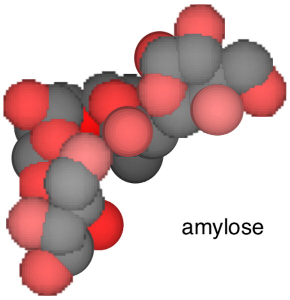
14

Carbohydrates



cellulose



amylose

CHAPTER SUMMARY

14.1 Chemical Nature of Carbohydrates - Polyhydroxy Aldehydes and Ketones

Carbohydrates are a class of organic biopolymers which consist of polyhydroxy aldehydes and ketones, their derivatives and polymers. Other terms for carbohydrates include sugars and saccharides. A single monomer unit is called a **monosaccharide**; several units are referred to as an **oligosaccharide**; larger polymers are called **polysaccharides**. The simplest carbohydrates are glyceraldehyde and dihydroxyacetone.

14.2 Nomenclature of Carbohydrates

The nomenclature of carbohydrates usually includes the suffix **-ose**. Monosaccharides may also be identified according to the nature of the carbonyl functional group (**aldose** or **ketose**), the number of carbons in the molecule (**tri-, tetr-, pent**- ose) or a combination of these two. Monosaccharides also have common names such as **ribose**, **glucose**, **galactose**, and **fructose** (four of the most common monosaccharides found in nature).

14.3 Structures of Monosaccharides

A. D,L - Aldoses: Open Chain Structures

Monosaccharides have one or more chiral carbon centers and can thereby form **enantiomers** and **diastereomers**. Most common monosaccharides are in the **D-family**. This means that, using D-glyceraldehyde as a starting point, other chiral carbons can be inserted between the carbonyl group and the D- carbon, producing families of diastereomers. If two monosaccharides differ in their structures by the configuration at only one chiral center, then they are called **epimers**.

CONNECTIONS 14.1 Diabetes

B. Ketoses

Ketoses are the functional isomers of the aldoses. A family of ketose structures can be generated in the same manner as aldoses.

C. Fischer Projections

The method of drawing saccharides in a vertical orientation with the most highly oxidized carbon at the top is called a **Fischer Projection**. It does not represent the real, three-dimensional structure of the molecule.

D. Cyclic Structures - Hemiacetal Formation

The carbonyl and alcohol groups within the same monosaccharide may react together if the carbon chain is long enough. The result is a **cyclic hemiacetal**. A new chiral center is formed at the carbon which was previously the carbonyl. The two optical isomers that can result are called **anomers**. Five- and six-membered cyclic structures predominate with the alcohol oxygen as the last member of the ring. These are referred to as **furanoses** and **pyranoses**, respectively. Cyclic structures exist in equilibrium with the open-chain form.

Haworth Formulas show the cyclic nature of monosaccharides with the -OH and -CH_2OH groups oriented up and down around a planar ring, that is, above and below the plane of the ring. **Conformational structures** more accurately illustrate the three-dimensional nature of cyclic monosaccharides, especially in the chair conformation of six-membered rings. The -OH and -CH_2OH groups are oriented in axial and equatorial positions around the ring and correspond to the up and down placement in a Haworth Formula. Anomeric isomers are designated as α**-** if the -OH group is down or axial or as β**-** if up or equatorial.

14.4 Some Reactions of Monosaccharides

A. Oxidation of Carbohydrates (Reducing Sugars)

The easy oxidation of the aldehyde group using a mild oxidizing agent such as copper (II) and silver (I) can detect the presence of carbohydrate. The carbohydrates are referred to as **reducing sugars**. This type of test cannot distinguish between aldoses and ketoses, however, because the alkaline conditions of the reaction lead to tautomerization of the ketone and immediate oxidation.

B. Reduction of Monosaccharides

The carbonyl group can be reduced to produce **sugar alcohols** such as sorbitol and mannitol.

C. Esterification

Also the alcohol groups may be esterified with a variety of acids including phosphoric acid. These **esters** are found extensively in metabolism.

CONNECTIONS 14.2 Prevention of Disease and Detoxification

14.5 Disaccharides and Polysaccharides

A. Glycosidic Linkages or Bonds

A reaction between one of the many alcohol groups on a monosaccharide with the hemiacetal group of an adjacent monosaccharide molecule to form an acetal is the method by which carbohydrates polymerize into disaccharides (sucrose and lactose), oligosaccharides, and polysaccharides such as starch, cellulose and glycogen. The α- or β- configuration of the anomeric carbon will be locked into position by this polymerization process. Not only does the diether linkage, called a **glycosidic bond**, resist oxidation by weak oxidizing agents (becoming **nonreducing sugars**) but it also is metabolically stable. Stereo-specific hydrolysis agents, known as enzymes, are required to cleave the glycoside.

B. Disaccharides

The most common disaccharides are lactose and sucrose. Lactose is found in milk and sucrose is table sugar from sugar cane and beets. Lactose is a reducing sugar while sucrose is not. Bacteria in animal mouths can use sucrose not only as food but also to form a cement which bonds the bacteria to the teeth - plaque.

CONNECTIONS 14.3 Low-Calorie Sweeteners

C. Polysaccharides

Starch, glycogen and cellulose are all polyglucose but differ in the nature of the glycosidic bonds, α- versus β-, and the positions of attachment.

Also the functions of these polysaccharides differ as do their commercial uses.

Nature produces variations in the functional groups of polysaccharides which gives rise to a diversity of overall structure and function. A good example is the A, B, O -blood type variation found in humans.

CONNECTIONS 14.4 Nitrocellulose and Rayon

Connections 14.4 summarizes the history and manufacture of the semi-synthetic materials rayon and nitrocellulose, both made from naturally occurring cellulose.

SOLUTIONS TO PROBLEMS

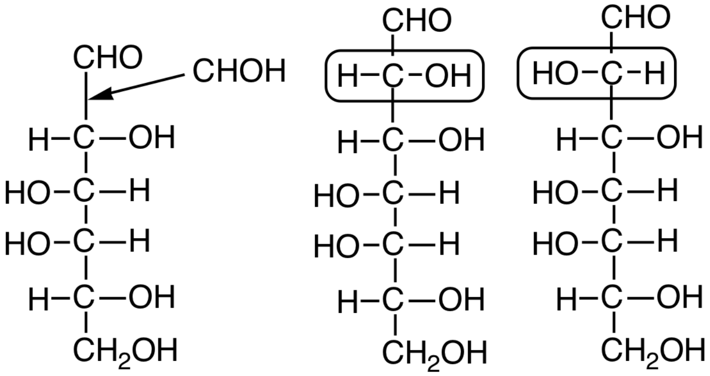
14.1 Nomenclature of Carbohydrates: Section 14.2

Allose is an aldohexose while xylose is an aldopentose.

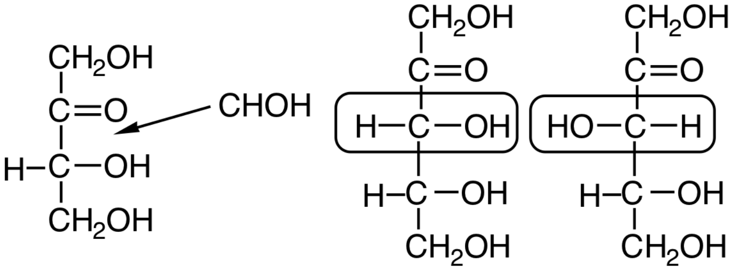
14.2 Structures of Monosaccharides: Section 14.3

Epimers have a different configuration at only one chiral carbon center. Epimers of D-glucose would be D-allose, D-mannose, and D-galactose. Diastereomers have different configurations at more than one chiral carbon center. Therefore any of the non-epimers of D-glucose would be diastereomers.

14.3 Structures of Monosaccharides: Section 14.3

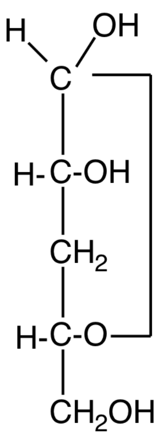


14.4 Structures of Monosaccharides: Section 14.1

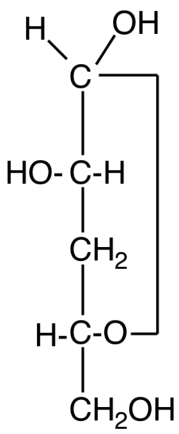


There are only two ketopentoses derived from D-erythrulose. They are epimers.

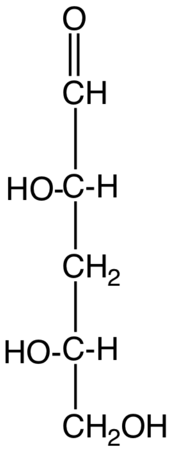
14.5 Structures of Monosaccharides: Section 14.3



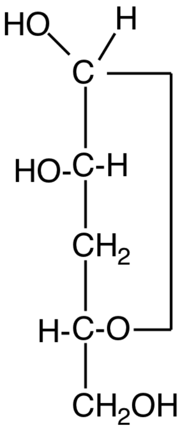
A



B



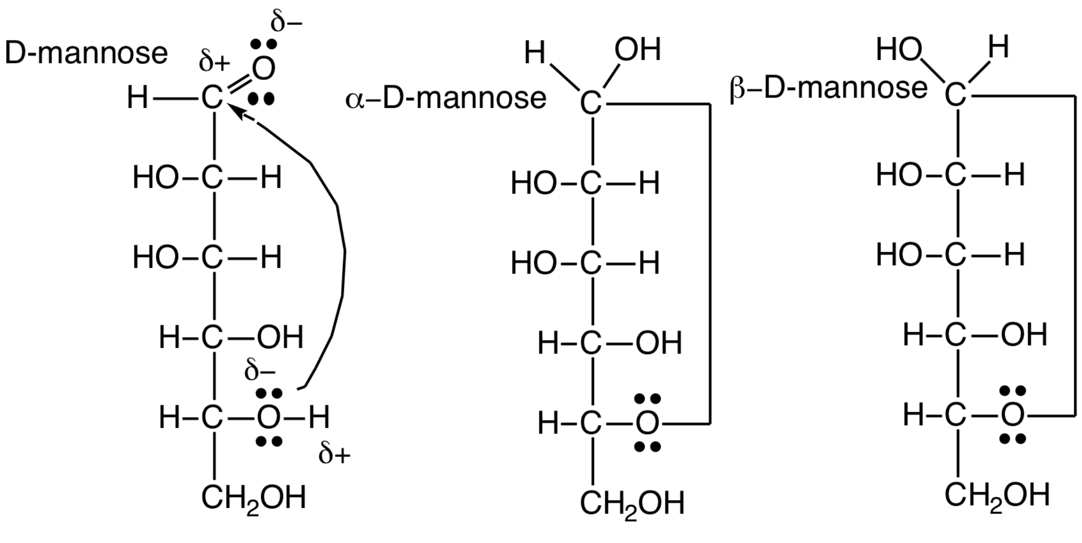
C

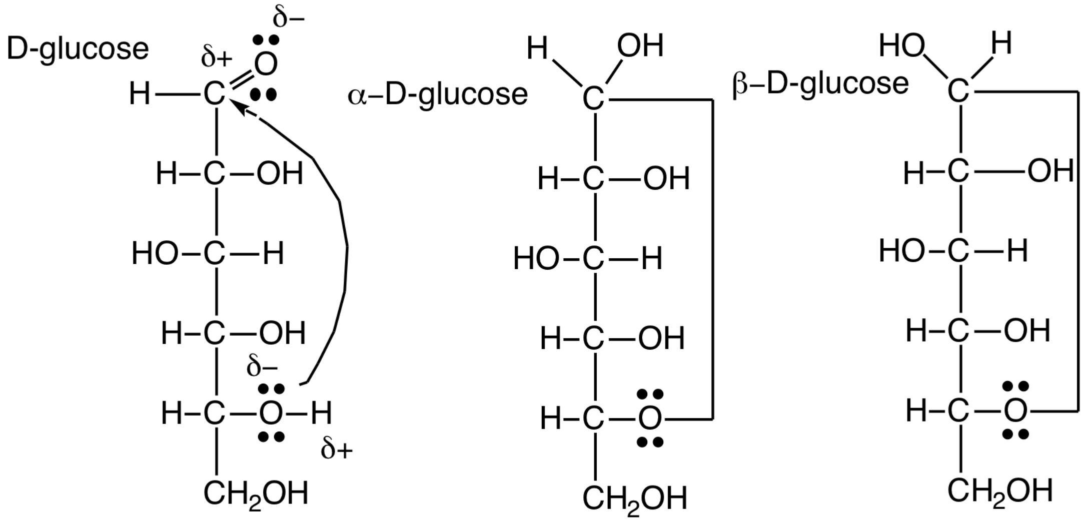


D

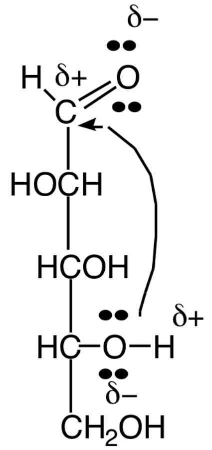
The epimers are **A** & **B**; the anomers are **B** & **D**; the diasteromers are **A** & **B**, **A** & **D**, **B** & **D**. Compound **C** could be an enantiomer to the open-chain form of A. In its current form, however, it doesn't have the same number of chiral carbon centers as do the other compounds.

14.6 Structures of Monosaccharides: Section 14.3D

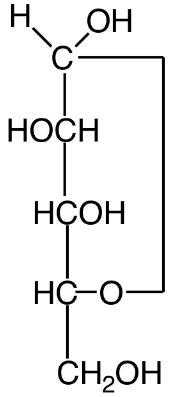




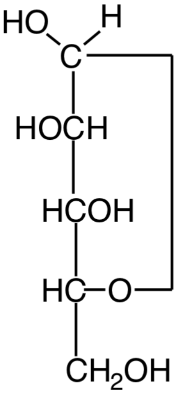
14.7 Structures of Monosaccharides: Section 14.3D



D-arabinose

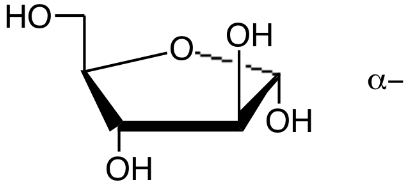


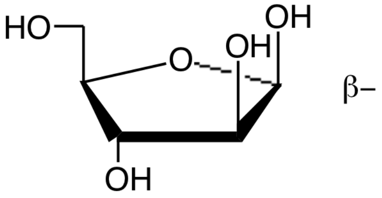
α−D-arabinose

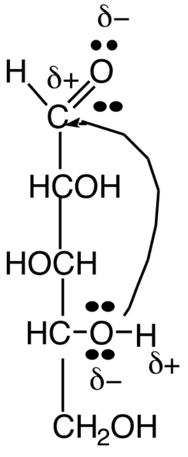


β−D-arabinose

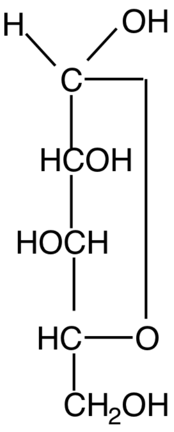
Five-membered rings



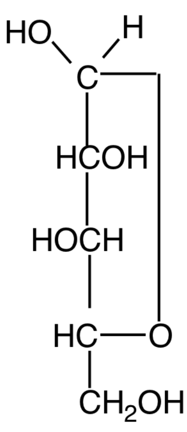




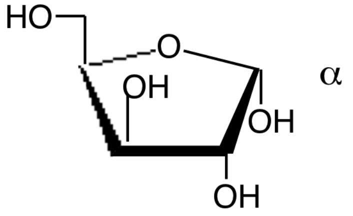
D-xylose

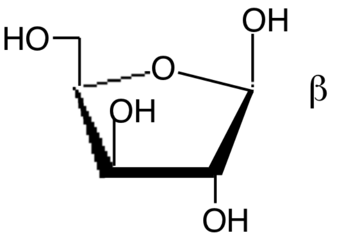


α−D-xylose

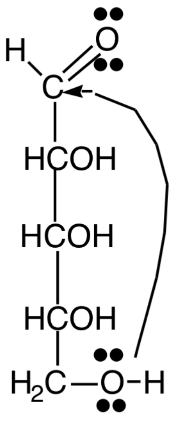


β−D-xylose

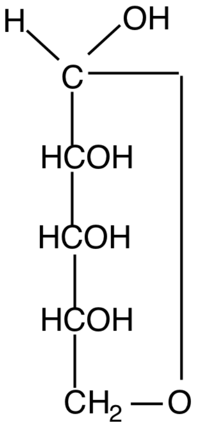




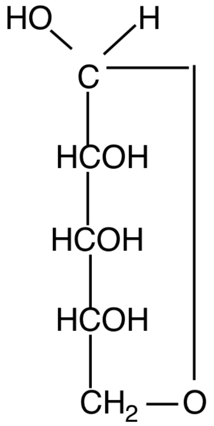
Six-membered rings



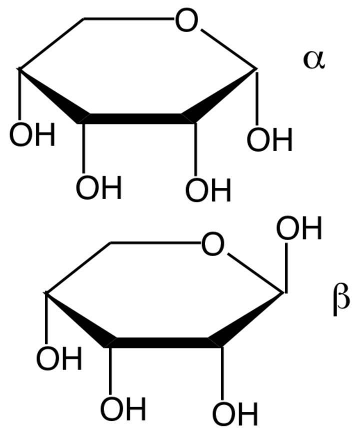
D-arabinose

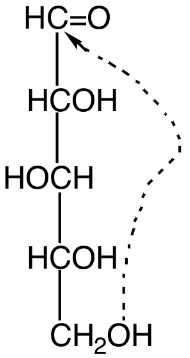


α–D-arabinose

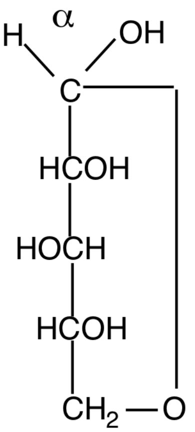


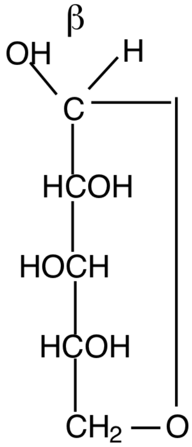
β–D-arabinose

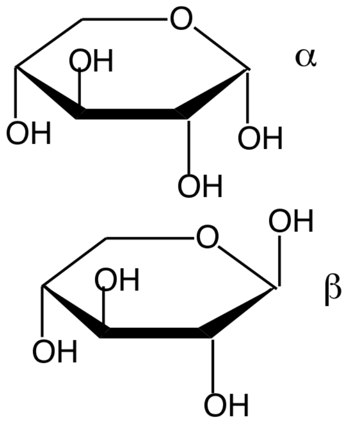




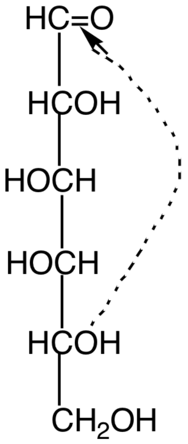
D-xylose



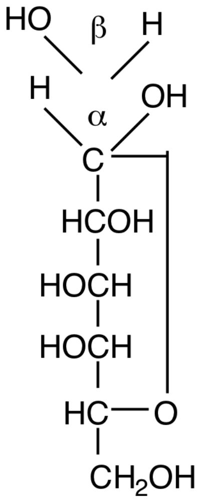




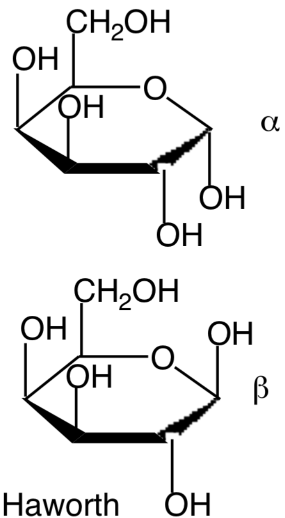
14.8 Structures of Monosaccharides (Cyclic and Open-chain Structures): Section 14.3



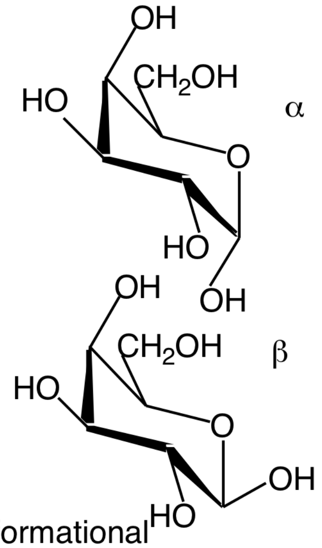
D-galactose



Fischer projection



Haworth Formulas



Conformational Structures

14.9 Structures of Monosaccharides (Cyclic and Open-chain Structures): Section 14.3

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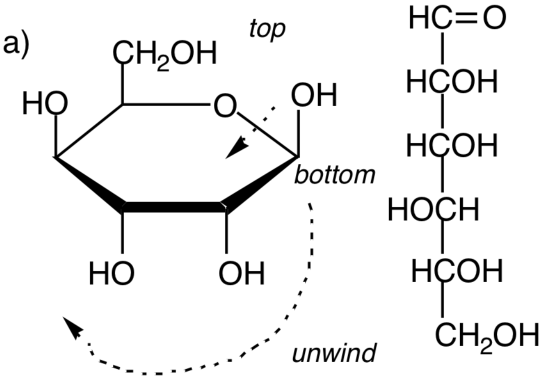

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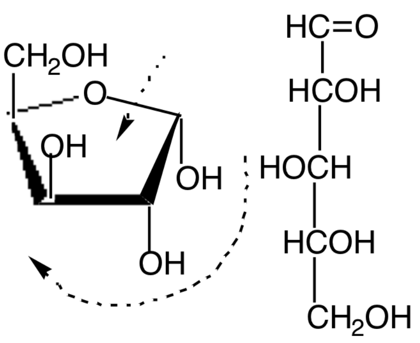
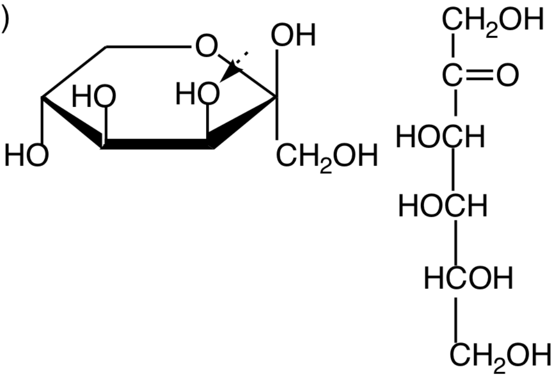
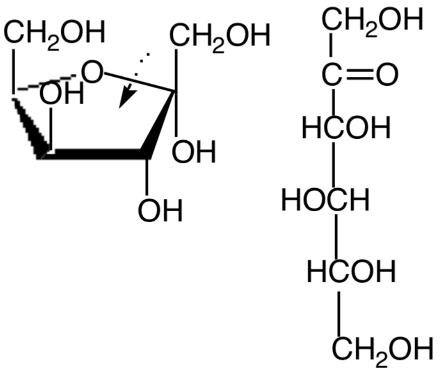


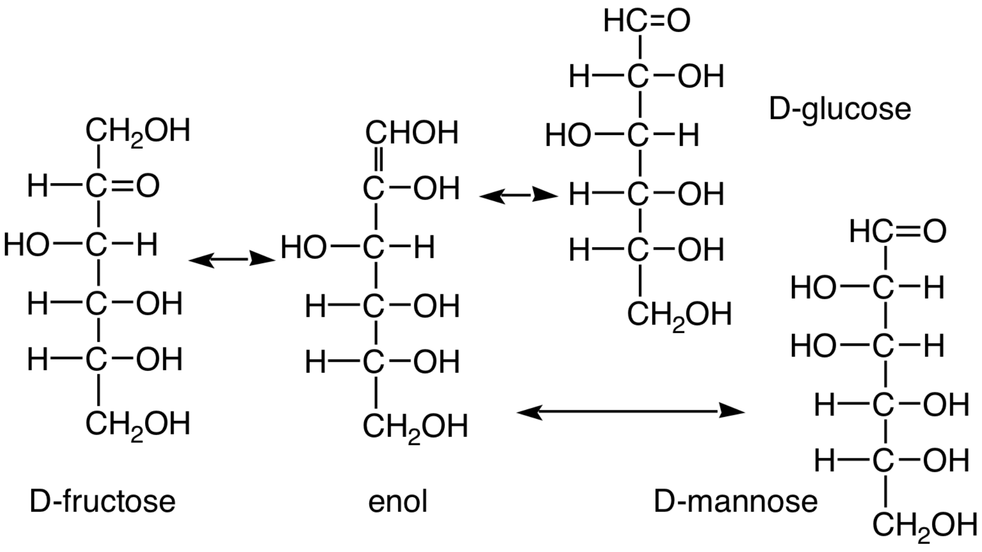
c)



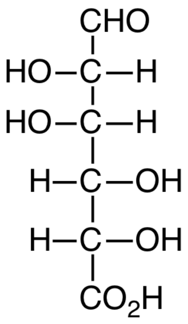
d)



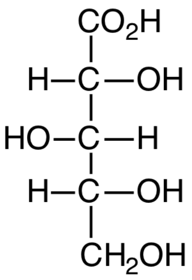
14.10 Some Reactions of Monosaccharides: Section 14.4



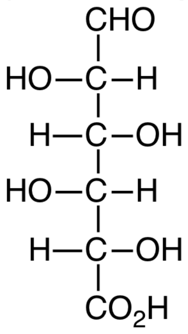
14.11 Some Reactions of Monosaccharides (Oxidation): Section 14.4



mannuronic acid
oxidized on C-6

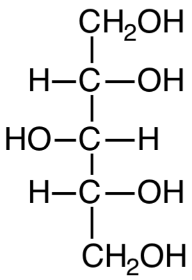


xylonic acid
oxidized on C-1

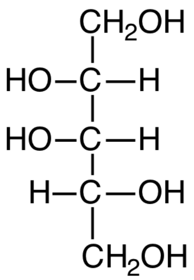


iduronic acid
oxidized on C-6

14.12 Some Reactions of Monosaccharides (Reduction): Section 14.4B



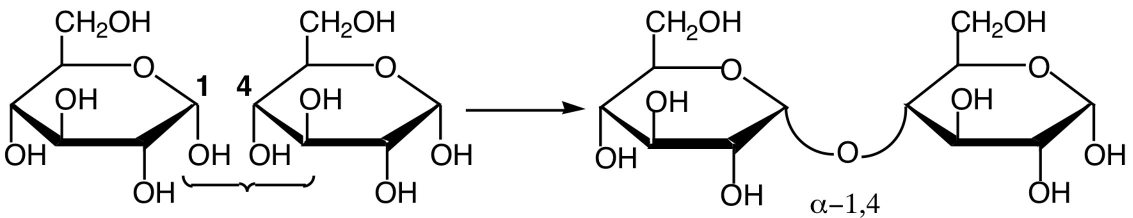
D-xylitol



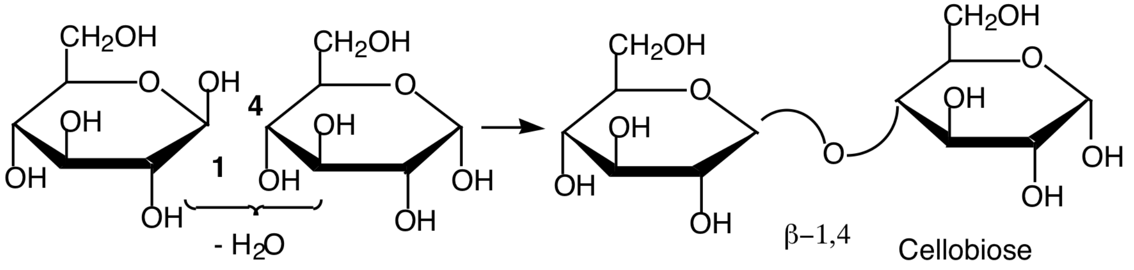
D-arabitol

Neither of these sugar alcohols is a reducing agent to Cu (II) or Ag (I) because they are not aldehydes nor are they 2-ketoses.

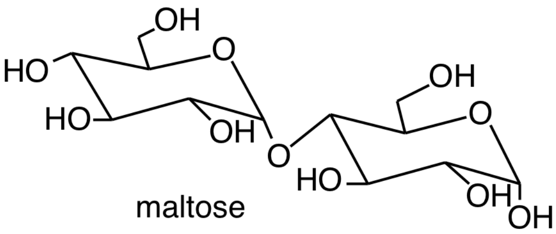
14.13 Disaccharides and Polysaccharides: Section 14.5

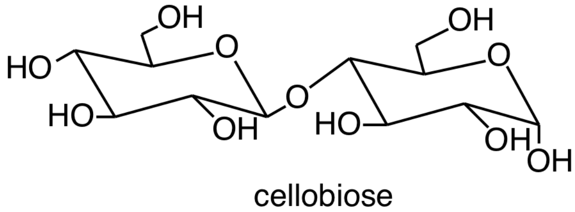


maltose



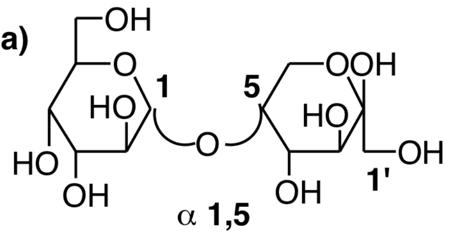
Cellobiose


maltose


cellobiose

14.14 Disaccharides and Polysaccharides (Glycosidic Linkages or Bonds): Section 14.5A

(a)



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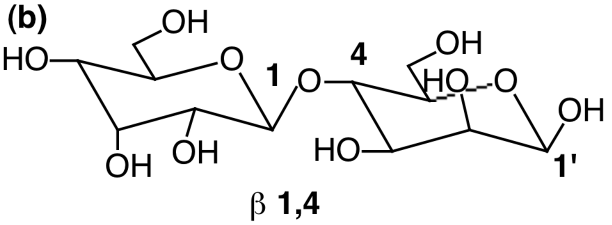

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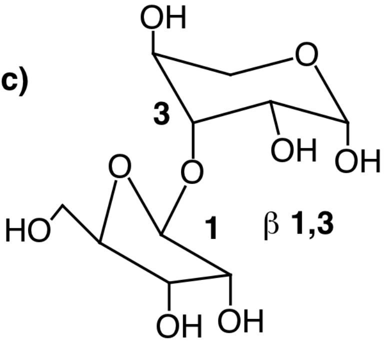

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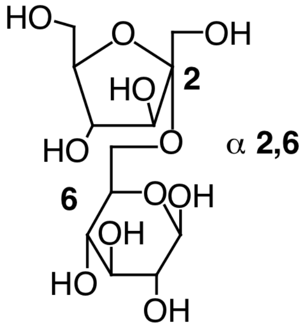
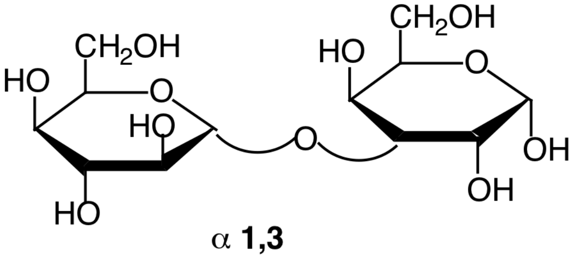
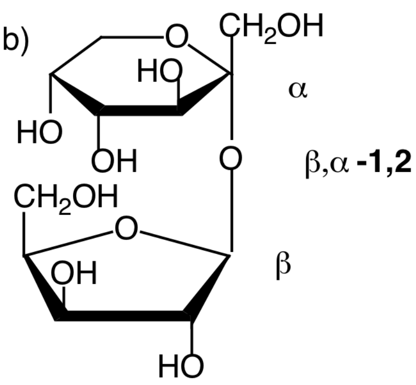


14.15 Disaccharides and Polysaccharides: Sections 14.5

a)



b)



14.16 Disaccharides and Polysaccharides: Sections 14.5

Besides the acetal and alcohol groups, chitin contains an amide. This group is neither acidic nor basic.

Heparin contains alcohol and acetal groups as well as acidic sulfonic acid and carboxyl groups.

14.17 Terms

a) A hexose is a six-carbon sugar while a pentose has five carbons.

b) An aldose has an aldehyde (RCH=O) functional group while a ketose has a ketone (RCOR).

c) A reducing sugar has an alcohol and ether functional groups on the same carbon. A nonreducing sugar is a diether.

d) Monosaccharides are small, single carbohydrate units, usually containing five or six carbons. Polysaccharides are polymers of monosaccharides linked by glycosidic bonds.

e) α- and β-D-glucose are anomers, that is, they are both the cyclic forms of glucose with opposite configurations for the -OH group attached to the new chiral center, the former carbonyl group.

f) Fischer projections are structures drawn vertically with the most oxidized carbon appearing at the top. They are not related spatially to real structures. Haworth formulas are cyclic carbohydrate structures in the form of cyclopentane and cyclohexane-type rings.

g) Amylose is the “linear” form of starch in which all of the glucose units are linked α-1,4 while amylopectin is branched, its main chain of glucose units linked through an α-1,4 glycosidic bond with α-1,6 bonded-branches about every 25 monomer units.

h) Glycogen is a polymer of glucose with a main chain having α-1,4 glycosidic bonds and α-1,6 branches every 8-10 units. Cellulose is polyglucose linked β-1,4.

i) Type 1 diabetes involves the absence or near absence of insulin to regulate body glucose concentrations. Type 2 diabetes is a more complicated condition in which insulin is usually present but not functioning properly.

j) Viscose rayon is a form of cellulose which has been processed by derivatization and reconstitution while acetate rayon is derivatized cellulose.

k) Fehling's test uses Cu (II) as a weak oxidizing agent while Tollen's test uses Ag (I).

14.18 Structure: Sections 14.3, 14.4 and 14.5

a) Cellobiose and maltose are both dimers of glucose and both are reducing sugars. Cellobiose has a β-1,4 glycosidic bond while maltose has an α-1,4 bond.

b) Galactose and glucose, linked β-1,4, are the units in the reducing sugar lactose. Sucrose is nonreducing because of the β,α-2,1 glycosidic bond between fructose and glucose.

c) α-D-glucose and α-D-galactose are epimers differing in the configuration about C-4. Both are reducing sugars.

d) α-D-glucose and α-D-fructose are reducing sugars and functional isomers of each other.

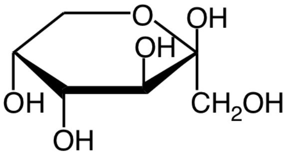
e) α-D-xylose and β-D-ribose are both aldopentoses and reducing sugars. They differ in configuration at C-1 of the cyclic form as well as at C-3.

f) Maltose has two glucose units linked α-1,4 while lactose is composed of galactose and glucose linked β-1,4; both are reducing.

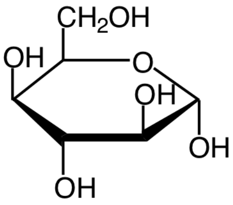
g) Cellulose is a linear polyglucose linked β-1,4 while starch consists of amylose (polyglucose α-1,4) and amylopectin (α-1,4 with α-1,6 branches). Both have reducing ends but not much would be seen with Fehling's or Tollen's tests because of the large molecular weight of both polymers.

14.19 Structure: Section 14.4

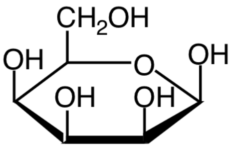
a) β-D-fructose



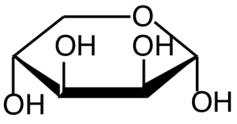
b) α-D-idose



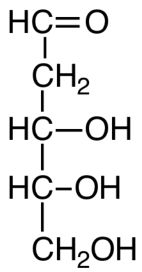
c) β-D-talose



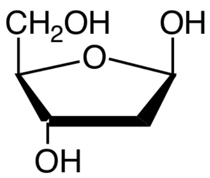
d) α-D-lyxose



14.20 Structure: Section 14.3

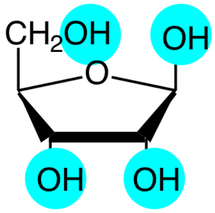


2-deoxyribose
open-chain form



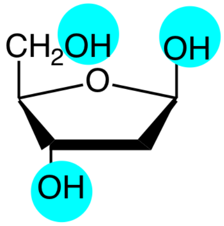
2-deoxyribose
Haworth form

14.21 Reactions: Section 14.4



ribose

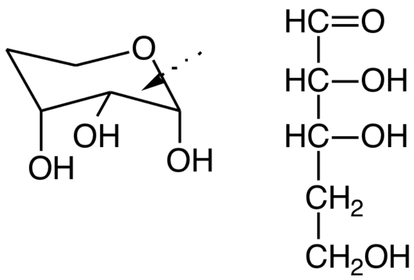
Ribose has 4 alcohol groups which can be esterified, while 2-deoxyribose has 3.



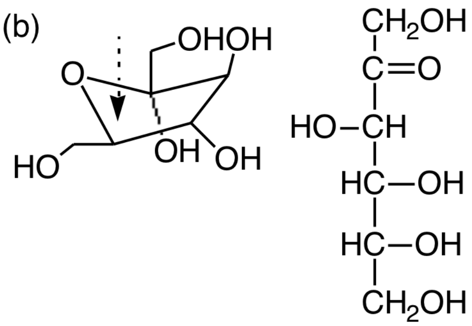
2-deoxyribose

14.22 Structure: Section 14.3

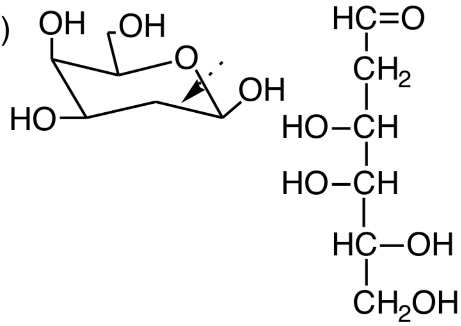
(a)



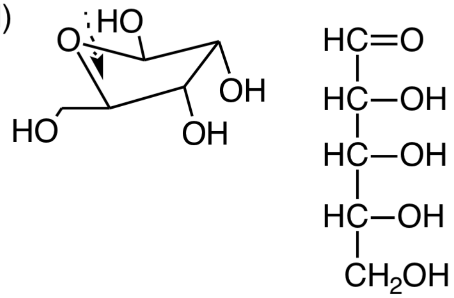
(b)



(c)

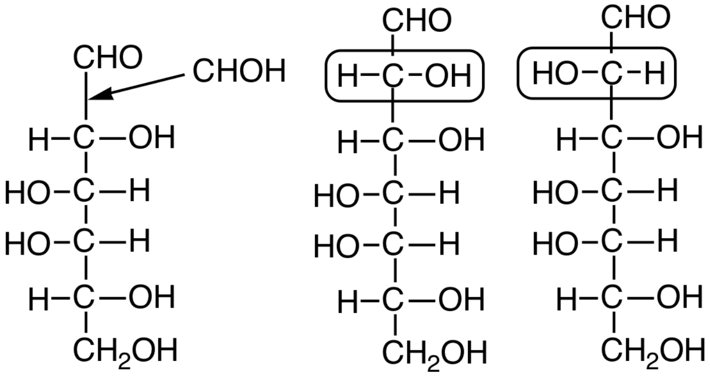


(d)



14.23 Optical Isomers: Section 14.3

There are two chiral carbons; four optical isomers are possible.



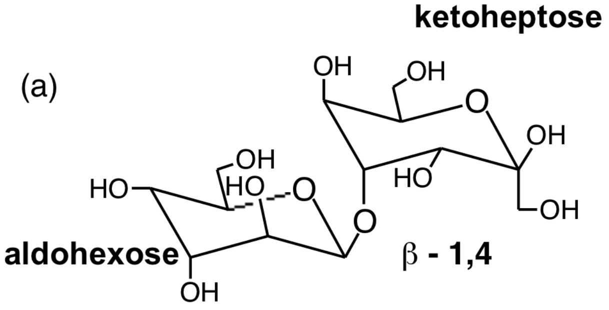
a/b are identical because you can rotate **b** in the plane of the page and it will superimpose on **a**. **a** is also obviously meso and is therefore not optically active. **c/d** are enantiomers. **a** is a diastereomer of **c** and **d**.

14.24 Reactions: Section 14.4

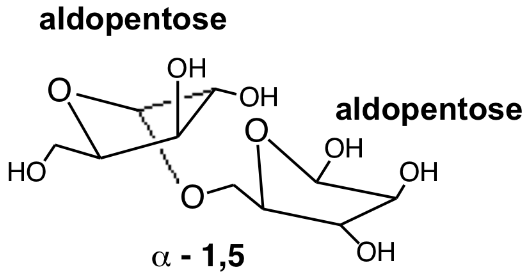
In the presence of acid, which also assumes an aqueous solution, the α– and β– forms of D-glucose will rapidly come into equilibrium with the open-chain aldehyde. Both the α– and β– anomers can react with methanol to form the methyl acetal.

14.25 Structure: Section 14.5

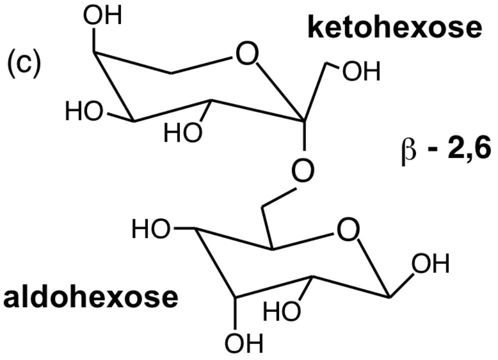
(a)



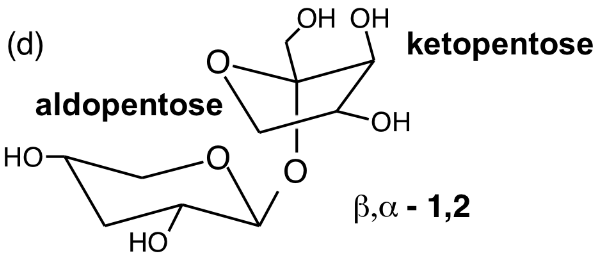
(b)



(c)



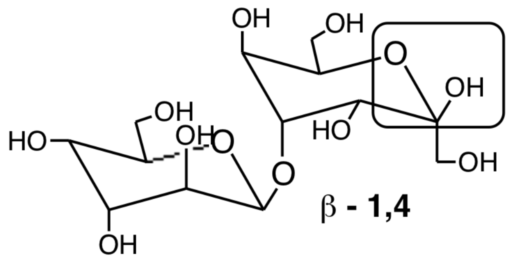
(d)



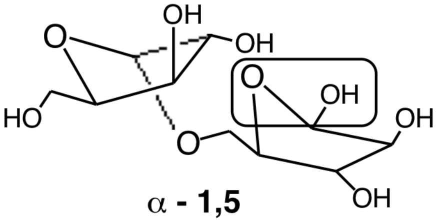
14.26 Reactions: Section 14.4

In the previous question, the first three, a,b,c, are reducing sugars. The d structure has both saccharides involved in an acetal-ketal linkage.

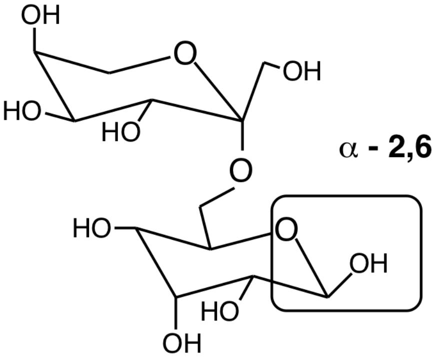
(a)



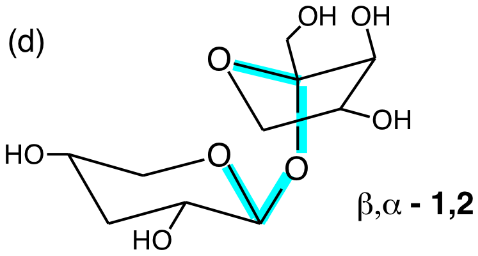
(b)



(c)

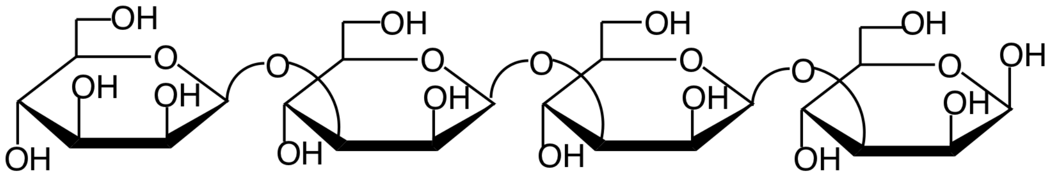


(d)

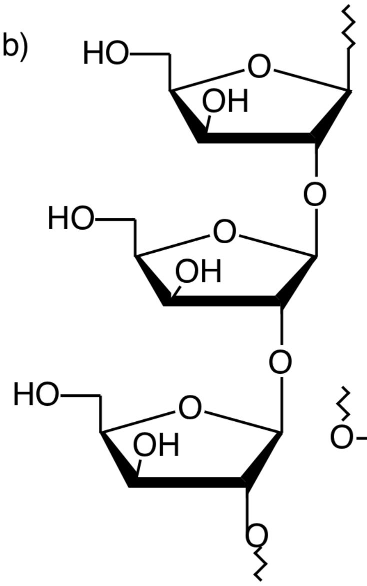


14.27 Structure: Section 14.5

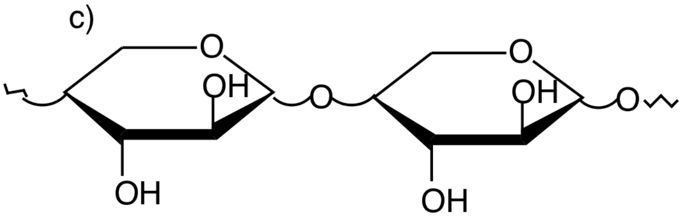
a)



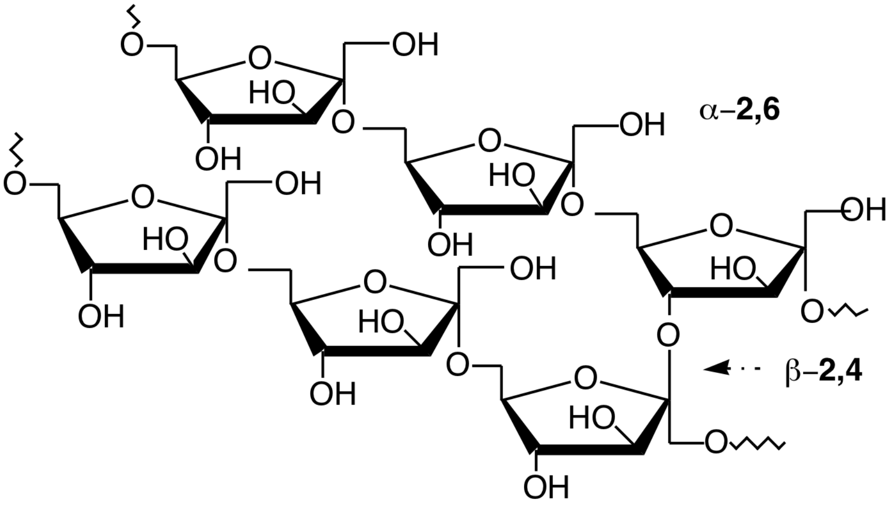
b)



c)

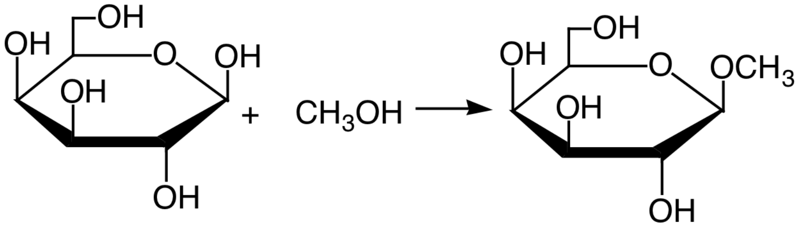


d)

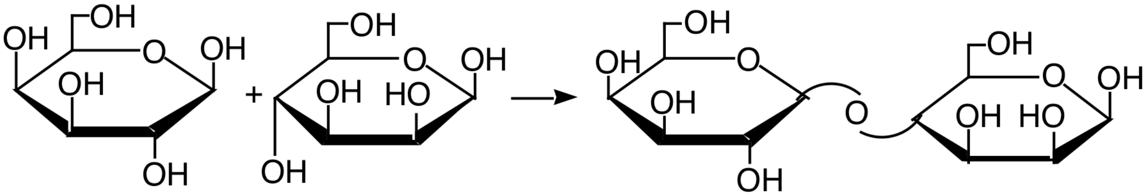


14.28 Reactions: Sections 14.4 and 14.5

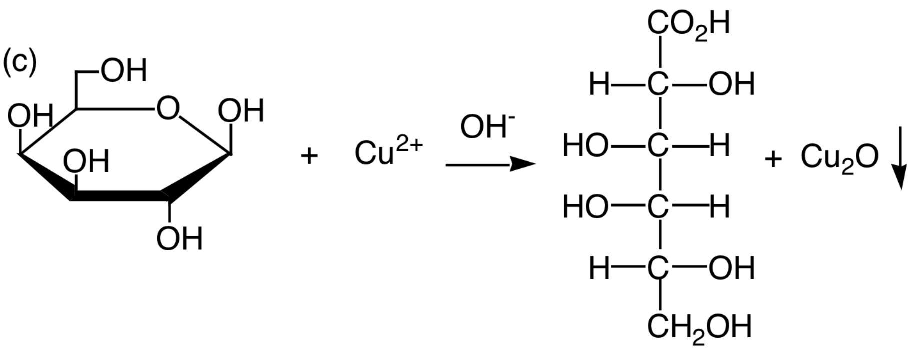
(a)



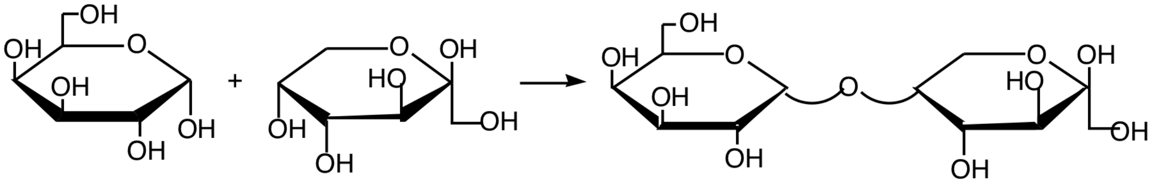
(b)



(c)



(d)



14.29 Reactions: Section 14.4

Fructose can tautomerize to glucose under the alkaline conditions of both the Fehling and Tollens tests. Therefore both fructose and glucose will test positive.

14.30 Reactions: Section 14.4

Since Fehling's test gives a positive result for any aldose or 2-ketose, it is evidence that there could be a sugar in urine but would not be a definitive test for glucose per se.